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Ship Materials Engineering Department

Research and Development Report

Effect of Lead Oxide and Titania on the Structure, Morphology and Superconductivity of Y–Ba–Cu–O Ceramic Materials

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A. Srinivasa Rao

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ABSTRACT

The effect of the addition of PbO and TiO_2, in the concentration range 0 - 15 wt. %, on crystal structure, morphology and superconductivity of $YBa_2Cu_3O_{6+x}$ was investigated. The results suggest that the addition of either TiO_2 or PbO (for PbO concentration above 3 wt.%) reduces the primary particle size of $YBa_2Cu_3O_{6+x}$. Both TiO_2 and PbO tends to stabilize the non superconducting tetragonal phase at the expense of superconducting orthorhombic phase of $YBa_2Cu_3O_{6+x}$. The orthorhombic - tetragonal phase transformation appears to be related to the additive induced oxygen depletion of $YBa_2Cu_3O_{6+x}$ to form Y_2BaCuO_y. Such a phase transformation process not only increases the normal state resistance of the superconductor, but also lowers the superconducting transition temperature.

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INTRODUCTION

The high temperature superconducting ceramic materials are limited in their application as bulk superconductors, because of the inherent problems that are associated with the processing of tough ceramic materials. Since all the ceramic materials show significant plastic deformation at different high temperatures, it is possible that high temperature deformation may be used in

forming high temperature superconductors into useful shapes. In an effort to extrude thin tapes or wires using superplastic deformation technology, this project was undertaken. For maximum superplastic deformation, it has been shown [1,3], that the grain size should be 100 - 500 nm. Therefore this study was aimed to investigate a method to produce fine particles of $YBa_2Cu_3O_{6+x}$ by incorporating different additives prior to the sintering process. In this paper, some of the results obtained for TiO_2 and PbO additions are presented.

EXPERIMENTAL PROCEDURE

Sample Preparation

The basic superconductor, $YBa_2Cu_3O_{6+x}$, was prepared by solid state chemical reaction of commercial yttrium oxide, copper oxide and barium carbonate. The superconducting Y-Ba-Cu-O ceramic powder obtained from the chemical reaction was ground into a fine powder in order to ensure stoichiometric homogeneity. Later, superconducting ceramic composites were produced by mixing predetermined amounts (in the range 0 - 15 wt.%) of either PbO or TiO_2) in a ball mill. The mixture was dry pressed into small discs which were later sintered. The general details of the processing of composites are exemplified in Figure 1, which shows a typical flow diagram of PbO / $YBa_2Cu_3O_{6+x}$ composite processing.

Measurements

The particle size and surface area of pure superconducting ceramic powder and the as obtained commercial powders was

determined using sedigraph and single point BET apparatus respectively. The additive distribution in the matrix of $YBa_2Cu_3O_{6+x}$ was determined using the scanning electron microprobe. The structure and morphology of all sintered samples was determined using x-ray diffraction, scanning and optical electron microscopy respectively. Indium solder was used to attach voltage and current leads to the specimens, so that the electrical resistance as a function of temperature could be measured by the four point method. The applied current was 10 milliamps and a nanovoltmeter with a sensitivity of 10^{-7} volts was used in the resistance measurement. In order to remove the effect of thermally induced voltage from the resistance readings, due care was taken by changing the sign of applied current at each reading.

RESULTS

The as-synthesized $YBa_2Cu_3O_{6+x}$ powder characteristics and the additive properties are given in Table 1. The results suggest that the as-synthesized superconducting ceramic powder density is comparable to the values reported in the literature. In addition, the results also indicate that as such the as-synthesized powder is not suitable for obtaining maximum superplastic deformation, however, it is suitable for a study on the effect of additives on the grain size control.

The morphology and the crystal structure of sintered $YBa_2Cu_3O_{6+x}$ suggests that the as-synthesized $YBa_2Cu_3O_{6+x}$ particles sinter to form long elongated rod like morphology and

orthorhombic crystal structure. Similar results have been reported in the literature for $YBa_2Cu_3O_{6+x}$ [4].

A typical morphology of sintered $YBa_2Cu_3O_{6+x}$ ceramic materials containing additives PbO and TiO_2 is shown in Figures 2 and 3 respectively. The results suggest that the addition of TiO_2 to the superconducting Y-Ba-Cu-O ceramic material significantly alter both the particle surface topography and the primary particle size. In addition the results also suggest that some diffusion of TiO_2 into $YBa_2Cu_3O_{6+x}$ grains also occurs during sintering above 920°C. The additive lead oxide neither produces significant physical change (except particle size reduction at high additive concentration) nor chemically diffuses into the grain structure of $YBa_2Cu_3O_{6+x}$.

In order to quantify the effect of the additives on particle size, a number of both optical and scanning electron micrographs (representing different areas of the whole sample) were obtained from polished samples as a function of additive concentration. From the micrographs, histograms were plotted in order to obtain the average particle size of the superconducting ceramic materials. Figure 4 shows the average particle size of $YBa_2Cu_3O_{6+x}$ in different composites. The results suggest that TiO_2 is very effective in reducing the particle size of $YBa_2Cu_3O_{6+x}$, and that the degree of grain size reduction increases with an increase in the additive concentration. Although additive PbO at lower concentrations (below 3 wt.%) did not affect $YBa_2Cu_3O_{6+x}$ grain size, at higher concentrations (above 3 wt.%) it tends to reduce the particle size.

The crystal structure of all $YBa_2Cu_3O_{6+x}$ samples containing the additives was determined and the details of the measurement procedure was reported elsewhere [5]. The results of the structural analysis suggest that the superconducting orthorhombic phase of the $YBa_2Cu_3O_{6+x}$ material decreases while the the tetragonal phase of the $YBa_2Cu_3O_{6+x}$ material increases with the addition of additives PbO and TiO_2. The examination of the x-ray diffraction patterns of PbO / $YBa_2Cu_3O_{6+x}$ composites revealed that the crystal structure also represents the structure of Y_2BaCuO_y and Pb_2O_3. However, their relative concentration depends upon the concentration of the additive (Figure 5). It is therefore possible that the oxygen liberated during the phase transformation of orthorhombic phase into tetragonal phase will be taken up by the additives in order to form a higher oxide (as in the case of PbO).

The electrical resistivity of all samples was measured as a function of sample temperature. From resistivity versus temperature plots, the superconducting onset temperature was determined. Figure 6 shows typical superconducting onset temperature versus additive concentration profiles for $PbO/YBa_2Cu_3O_{6+x}$ and $TiO_2/YBa_2Cu_3O_{6+x}$ composites. The results suggest that the superconducting transition temperature (T_c) of samples containing PbO and TiO_2 decreases very sharply with an increase in the additive concentration. The results also suggest that for PbO / $YBa_2Cu_3O_{6+x}$ composite system, once, a critical T_c value 40 K) is reached, the additive concentration

has very little effect on the T_c. However, the studies with TiO_2 indicate that the addition of TiO_2 has a very adverse effect on the T_c of the composite. It is possible that the diffusion of TiO_2 into the grain structure of $YBa_2Cu_3O_{6+x}$ (Figure 3) and/ or the formation of a different ceramic species with TiO_2 is responsible for the deterioration of the electrical properties of $YBa_2Cu_3O_{6+x}$. In addition, it was also found that the resistivity normal state resistance of the composites increases with an increase in the additive concentration.

DISCUSSION

The control of the microstructure is essential for the development of both mechanical and electrical properties of high temperature superconductors. In general for superplastic flow, the important requirements are (1) very small particle size, and (2) the retention of original crystal structure even after the deformation. Although, chemical coprecipitation methods often produce very fine particles, those methods are very tedious and time consuming. The present investigation clearly demonstrates that the addition of 15 wt. % TiO_2 to $YBa_2Cu_3O_{6+x}$ prior to the sintering process will not only inhibit grain growth (Figures 4 and 5), but also decrease the primary particle size (Table 1). Although the present study could not demonstrate that the additives will not affect the crystal structure or the superconducting properties, it has given enough evidence to postulate a mechanism for the degeneration of the superconducting properties of $YBa_2Cu_3O_{6+x}$ in the composite (viz. the process of removal of oxygen from $YBa_2Cu_3O_{6+x}$ followed by

its migration into the vicinity of the additive). It is therefore possible that a proper selection of the additive on the basis of its chemical inertness towards $YBa_2Cu_3O_{6+x}$, may produce preform consisting of fine particles of superconducting ceramic that is suitable for superplastic deformation.

CONCLUSION

From the present investigation the following conclusions can be made :

1. Sintered $YBa_2Cu_3O_{6+x}$ superconducting ceramic preforms with small particle size can be produced by solid state chemical reaction method with the addition of titania.

2. The reduction in the primary particle size of $YBa_2Cu_3O_{6+x}$ increases with an increase in the additive (TiO_2 and $\geq$ 3 wt.% PbO) concentration. The effect of additive on the particle size of $YBa_2Cu_3O_{6+x}$ in composites containing < 3 wt.% PbO is not very significant.

3. The addition of TiO_2 and PbO not only lowers the superconducting transition temperature of the bulk superconductor, but also alters the crystal structure of $YBa_2Cu_3O_{6+x}$ (the superconducting orthorhombic crystal phase decreases while these additives tend to stabilize the non superconducting tetragonal phase).

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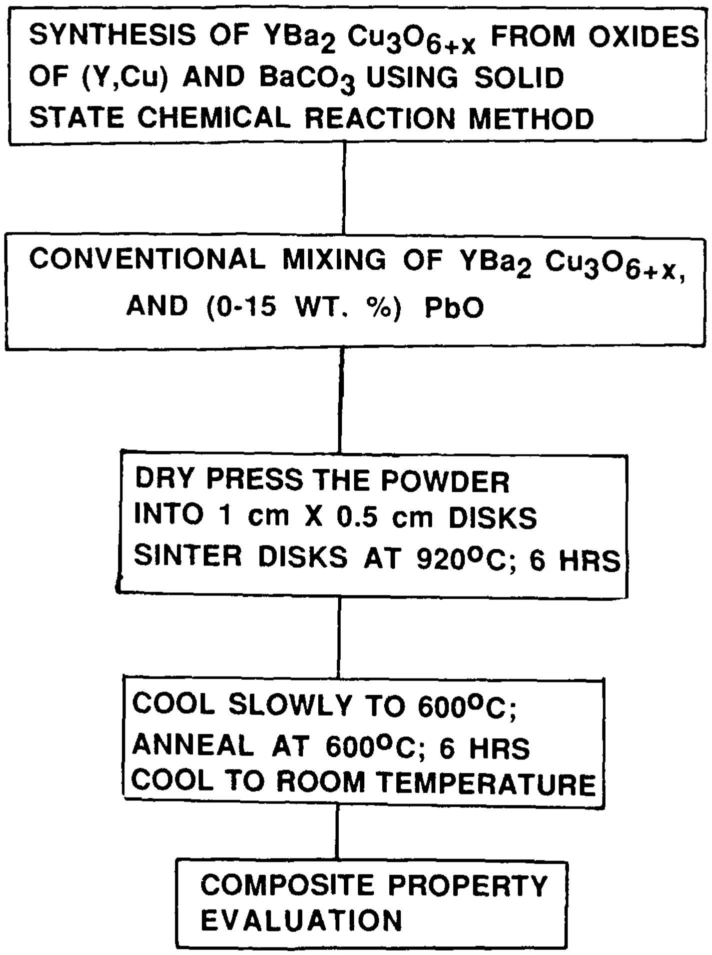

Figure 1. Flow diagram of the processing of PbO / $YBa_2Cu_3O_{6+x}$ composites.

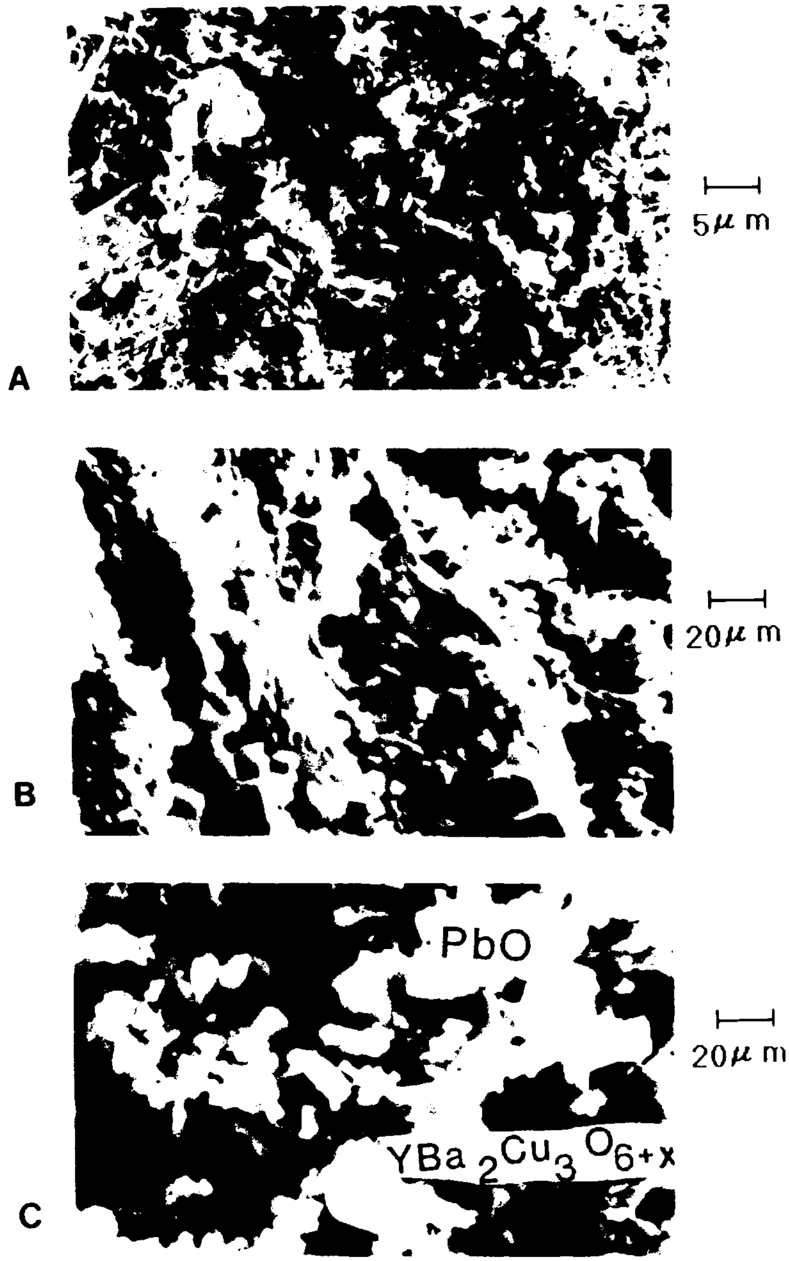

Figure 2. Morphology of sintered PbO / $YBa_2Cu_3O_{6+x}$ ceramic composite containing (A) 3, (B) 5 and (C) 10 wt.% PbO respectively.

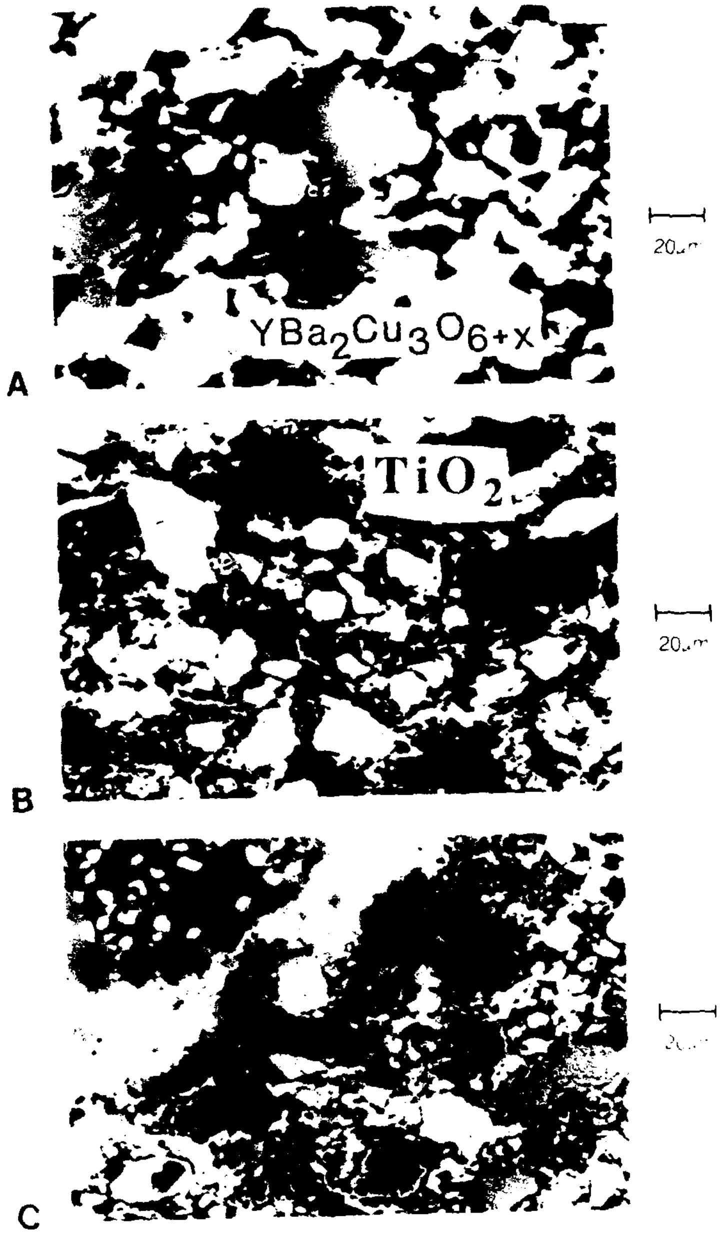

Figure 3. Morphology of sintered TiO_2 / $YBa_2Cu_3O_{6+x}$ ceramic composite containing (A) 2, (B) 5 and (C) 10 wt.% TiO_2 respectively.

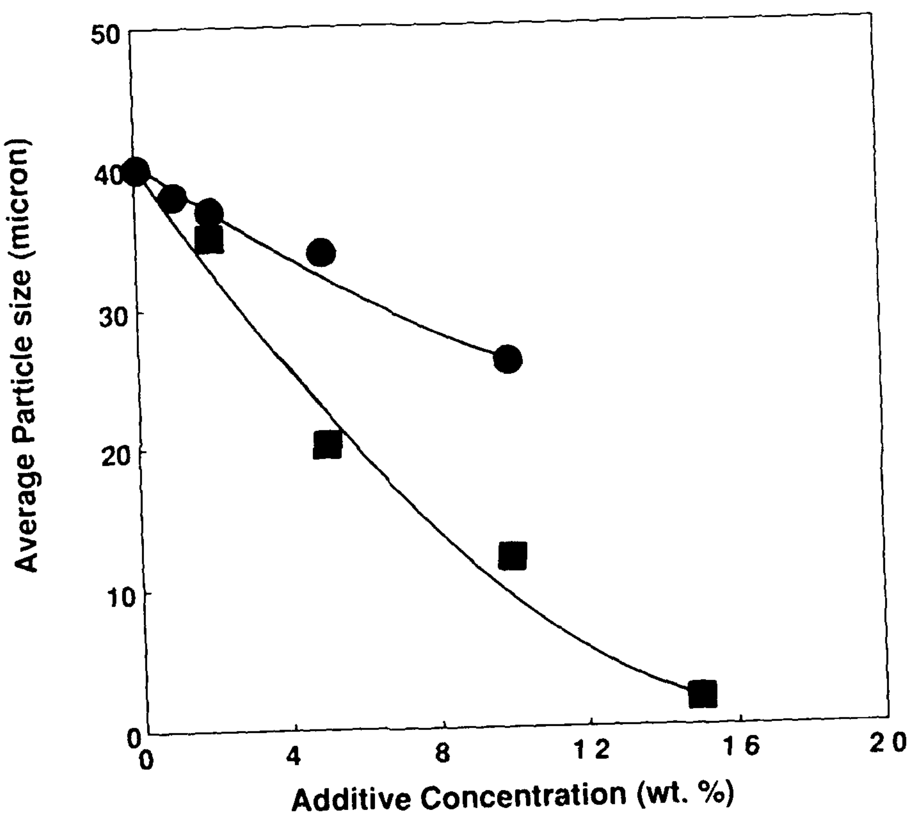

Figure 4. $YBa_2Cu_3O_{6+x}$ particle size distribution versus (●) PbO and (■) TiO_2 concentration of sintered composite samples.

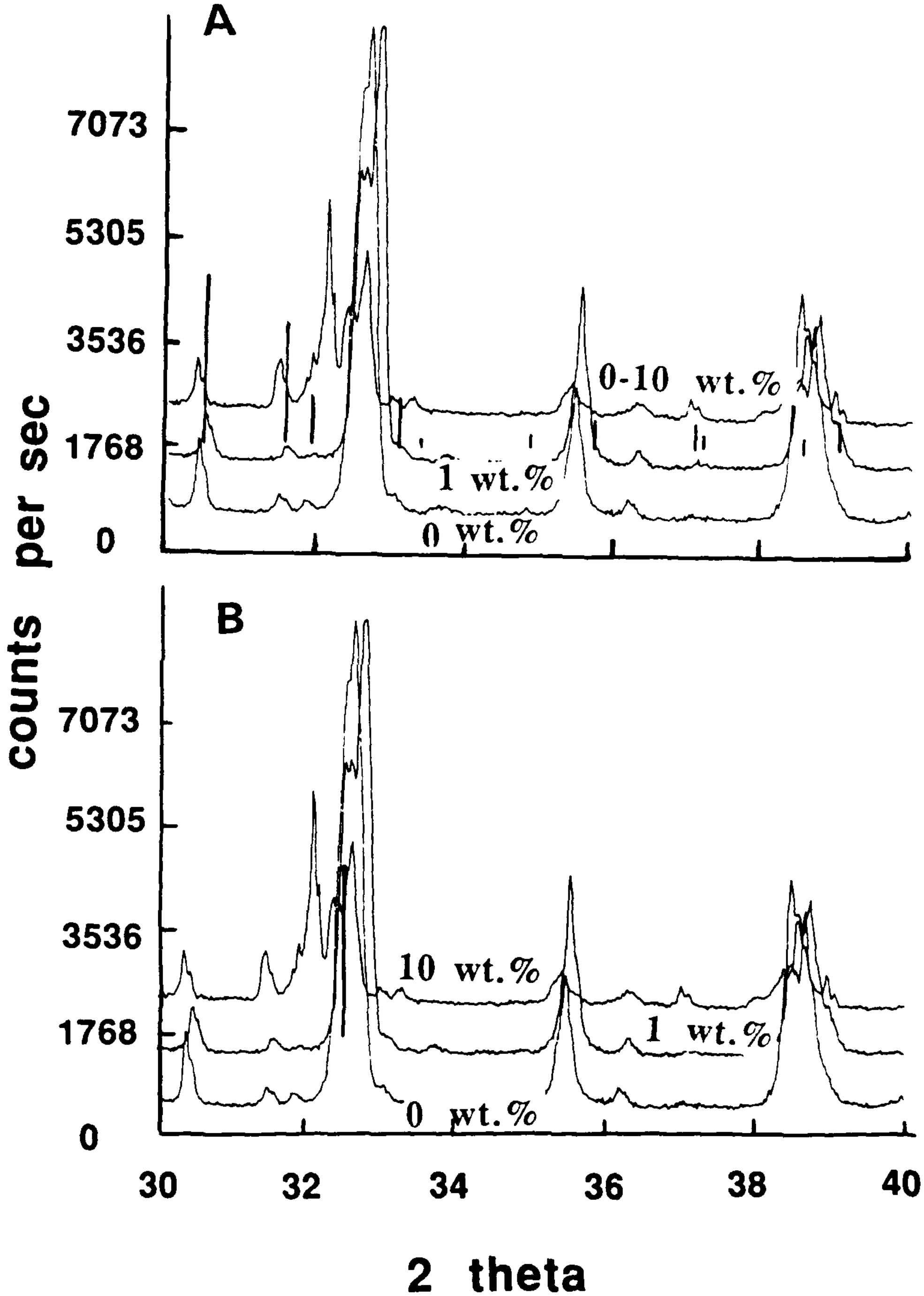

Figure 5. Wide angle x - ray diffraction patterns of 0, 1 and 10 wt.% PbO / $YBa_2Cu_3O_{6+x}$ Composites. Also high lighted are some important standard peaks for (A) Y_2BaCuO_5 and (B) Pb_2O_3.

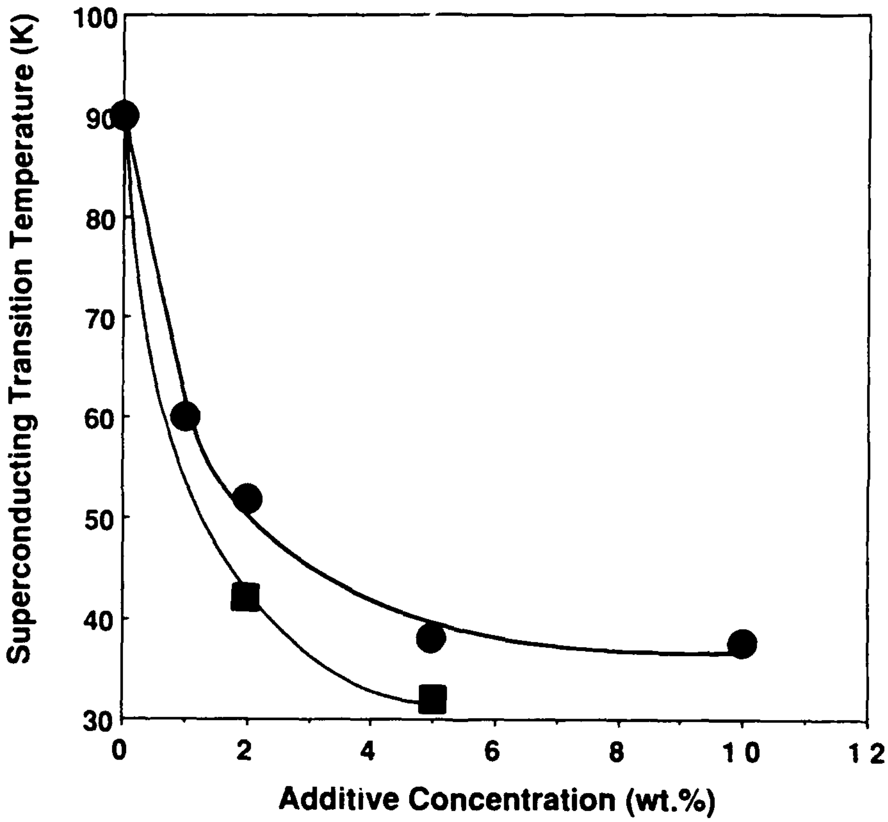

Figure 6. Superconducting transition temperature versus (●) PbO and (■) TiO_2 concentration of sintered $YBa_2Cu_3O_{6+x}$ composites.

Table 1. AS – Synthesized Yttrium, Barium and Copper Oxide Powder Properties

density (gm/c.c)	6.0
average particle size (microns)*	- 10.0
surface area (m^2/gm)+	0.22

* Particle size measurement using Sedigraph

\+ Surface area measurement using single point BET apparatus

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The effect of the addition of PbO and TiO_2, in the concentration range 0 - 15 wt.%, on crystal structure, morphology and superconductivity of $YBa_2Cu_3O_{6+X}$ was investigated. The results suggest that the addition of either TiO_2 or PbO (for PbO concentration above 3 wt.%) reduces the primary particle size of $YBa_2Cu_3O_{6+X}$. Both TiO_2 and PbO tends to stabilize the non superconducting tetragonal phase at the expense of superconducting orthorhombic phase of $YBa_2Cu_3O_{6+X}$. the orthorhombic - tetragonal phase transformation appears to be related to the additive induced oxygen depletion of $YBa_2Cu_3O_{6+X}$ to form Y_2BaCuO_y. Such a phase transformationprocess not only increases the normal state resistance of the superconductor, but also lowers the superconducting transition temperature.

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